XAFS Studies with Palladium after Reaction with Dissolved Tetraphenylborate

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Introduction: Removal of radioactive Cs by precipitation with dissolved tetraphenylborate (TPB) from High-Level Radioactive Waste (HLW, the waste product associated with the dissolution of spent fuel rods for the recovery of plutonium) is being re-considered as a waste treatment strategy at the U.S. DOE Savannah River Site (SRS). At the SRS, approximately 200 million-L of this extremely radioactive material resides in 49 subsurface tanks and awaits treatment. Previous attempts to treat HLW tanks at the SRS with dissolved TPB resulted in the evolution of benzene (a product of TPB decomposition), at levels that did not permit the safe operation of the facility at design throughput rates. Although low levels of benzene from radiolytic decomposition were anticipated during the previous attempt to treat the waste, the amount of benzene was underestimated. The HLW tanks, which contain every element in the periodic chart (as the stable and radioactively unstable products of nuclear fission), are thought to contain catalytic metals that are capable of decomposing TPB. Studies with HLW simulants identified Pd [added as dissolved Pd(II)] to be highly reactive towards the decomposition of dissolved TPB.

Methods and Materials: The Pd-containing HLW simulants were prepared by addition of dissolved Pd(II) to a mixture of diphenylmercury, NaOH and TPB decomposition products. The mixtures were heated overnight in a water bath and then filtered in a N_2 atmosphere. The solids were prepared for Pd K-edge EXAFS measurements in $N_{2(g)}$ by placing the filter cake in plastic sample holders with double polypropylene windows. The samples were put in vacuum-sealed plastic bags and placed in sealed Mason jars until EXAFS analysis. X-ray absorption was monitored using florescence and transmission detection modes simultaneously.

Results: Based on comparison to FCC Pd metal foil, FCC metallic Pd was present in all samples. Higher shell metal atoms were visible out to 6 Å. Model fits confirm the samples contained FCC Pd metal clusters with an average coordination number of 5 to 7 (depending on treatment)--with Pd-Pd first shell bond lengths of 2.77 Å. FCC Pd in an infinite lattice should contain a coordination number (CN) of 12 and thus a lower CN exhibited by the samples allows an estimate of cluster size to be made. Based on previously published maximum *mnp* site indices, clusters with an average CN of 5 and 7 would have an average diameter of 4 to 9 Å respectively (Kodre et al. 1999). This would correspond to Pd being present as a nanocluster. In addition to Pd in the first shell, one or more low atomic weight atoms (such as O, C or Na, an exact determination of atom identity was not possible) with having a total CN of 1 were present in the first shell. Analytical techniques such as wet chemical methods [to determine TPB degradation rates and the Pd solid phase concentration], scanning electron microscopy and transmission electron microscopy were also used to characterize the Pd. Collectively, these techniques confirm the reduction of dissolved Pd(II) to Pd metal and the formation of Pd nanoclusters.

Conclusions: Due to their small size, the metal clusters are likely to have high catalytic activities and therefore promote TPB degradation. To date, only studies with HLW simulants have been performed. We anticipate that similar studies with HLW materials will be performed in 2001.

References: A. Kodre, I, Arčon, J., Batista, and A. Pintar. "EXAFS analysis of Pd atomic clusters," J. Synchr. Rad. *6*, 458-459, 1999.